Electronic Supporting Information

A novel Na$_3$La(PO$_4$)$_2$/LaPO$_4$:Eu blue-red dual-emitting phosphor with high thermal stability for plant growth lighting

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Fig.S1. XRD pattern of pure-phase LaPO$_4$, pure-phase Na$_3$La(PO$_4$)$_2$, and three samples of diphasic phosphors at different sintering time.

In order to obtain the pure-phase Na$_3$La$_2$(PO$_4$)$_3$, we have tried other sintering
condition, including two-step method. First, to prepare pure-phase Na$_3$La(PO$_4$)$_2$ and LaPO$_4$, the reactions involved are as follows:

$$3\text{Na}_2\text{CO}_3 + \text{La}_2\text{O}_3 + 4\text{NH}_4\text{H}_2\text{PO}_4 \rightarrow \text{Na}_3\text{La(PO}_4)_2 + 3\text{CO}_2 + 4\text{NH}_3 + 6\text{H}_2\text{O} \quad (1)$$

$$\text{La}_2\text{O}_3 + 2\text{NH}_4\text{H}_2\text{PO}_4 \rightarrow 2\text{LaPO}_4 + 2\text{NH}_3 + 3\text{H}_2\text{O} \quad (2)$$

Then, Na$_3$La(PO$_4$)$_2$ and LaPO$_4$ were mixed by stoichiometric ratio, boric acid acting as flux was added, and the mixture was sintered for 12 h, 36 h and 72 h. The XRD patterns are shown in Fig. S1. The three samples are all composed of Na$_3$La(PO$_4$)$_2$ and LaPO$_4$ phases. The crystallinity of samples changes with the increase of calcination time, but there was no new phase formed. Results indicates that the reaction (3) did not happen.

$$\text{Na}_3\text{La(PO}_4)_3 + \text{LaPO}_4 \rightarrow \text{Na}_3\text{La}_2(\text{PO}_4)_3 \quad \text{(nonreactive)} \quad (3)$$

Thus, we conclude that Na$_3$La(PO$_4$)$_2$ did not react with LaPO$_4$, and no Na$_3$La$_2$(PO$_4$)$_3$ phase was formed.

**Fig. S2.** (a) SEM image, (b-f) elemental mapping and (f) EDX spectrum of NLP:0.02Eu phosphors.
Fig. S3 (a) Diffuse reflection spectra of LaPO$_4$, LaPO$_4$:Eu, Na$_3$La(PO$_4$)$_2$ and Na$_3$La(PO$_4$)$_2$:Eu samples. (b) the plot of $(ahv)^2$ versus $hv$ based on the samples.

According to the diffuse reflection spectra, the band gap of pure-phase LaPO$_4$, LaPO$_4$:Eu, Na$_3$La(PO$_4$)$_2$ and Na$_3$La(PO$_4$)$_2$:Eu samples were calculated to be 5.15, 5.10, 4.95 and 5.07 eV, respectively, as shown in Fig. S3. In pure-phase LaPO$_4$ and Na$_3$La(PO$_4$)$_2$, the band gap after Eu-doping showed little change (LaPO$_4$, reduce from 5.15 to 5.10 eV; Na$_3$La(PO$_4$)$_2$, increase from 4.95 to 5.07 eV)

Fig. S4. Excitation line of BaSO$_4$ reference and emission spectrum of NLP:0.02Eu phosphor characterized by using an integrating sphere.
For photo-luminescence application, the importance of quantum efficiency (QE) should be considered. According to the method described by De Mello et al., QE can be calculated by the following equation:

\[
\eta = \frac{\int L_S}{\int E_R - \int E_S}
\]

where \( L_S \) is the emission of the sample, \( E_S \) equals to the spectrum of the sample excited by the light, and \( E_R \) represents the spectrum of the excitation light without the sample. The results are listed in Fig. S3. Under 266 nm excitation, the calculated QE of NLP: 0.02Eu is 39.70%.

![Emission spectra](image)

**Fig. S5.** Emission spectra (\( \lambda_{ex} = 266 \) nm) of La\(_{1-x}\)PO\(_4\):xEu phosphors.
**Fig. S6.** Emission spectra ($\lambda_{\text{ex}} = 266$ nm) of Na$_3$La$_{2-x}$(PO$_4$)$_3$:xEu phosphors.

**Fig. S7.** The emission spectra of LaPO$_4$ @Na$_3$La(PO$_4$)$_2$:Eu two-phase phosphor (blue line) and mix the two single-phase phosphors LaPO$_4$:Eu and Na$_3$La(PO$_4$)$_2$:Eu (red line).
**Fig. S8.** The temperature dependent spectrum of (a) Na$_3$La(PO$_4$)$_2$:0.02Eu and (b) Na$_{2.7}$Li$_{0.3}$La(PO$_4$)$_2$:0.02Eu phosphor excited at 266 nm. The illustration shows the variety of relative luminescence intensity at 422 nm and 594 nm with temperature.

**Notes and references**